# LXVII.--On the Sulphides of Vanadium.

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In his well-known research on vanadium, published in 1831, Berzelius (*Pogg. Ann.*, **22**, 1) describes two sulphides :—

(1.) Vanadinsvalighet, VS<sub>2</sub>,

(2.) Vanadinsvafla, VS<sub>3</sub>,

the English names for these substances being-(1) Vanadium bisulphide, and (2) Vanadium persulphide.

No addition of importance was made to our knowledge concerning the chemistry of vanadium until Roscoe (*Phil. Trans.*, 1868, 1; 1869, 679; 1870, 317) in 1867—70 published his investigations on the subject, revolutionising our views concerning vanadium and its compounds by proving that the substance hitherto supposed to be the metal is an oxide, and that consequently all the compounds described by Berzelius must also contain oxygen.

Roscoe at the same time found it necessary, from considerations of the chemical relationships of vanadium, to take its atomic weight at one-half that previously assigned to it, and the double correction of Berzelius's formulæ is effected by the substitution in them of the expression V by the one  $V_2O_2$ .

It is, however, a singular fact that whilst this correction has been applied to the other vanadium compounds, the sulphides have in most treatises and dictionaries of chemistry been described as nonoxygenated products, having the formulæ  $V_2S_4$  and  $V_2S_5$  [= $(V_2S_2)S_2$ and  $(V_2S_2)S_3$ ]. In one or two instances, however, Berzelius's formulæ have been correctly translated into their modern equivalents,  $(V_2O_2)S_2$ and  $(V_2O_2)S_3$ .

If, on the one hand, these compounds prepared by Berzelius are oxysulphides, it is as well that the fact should be distinctly recognised; whilst, on the other hand, if they are true sulphides, they acquire a special interest as forming the only series of non-oxygenated vanadium compounds obtained by Berzelius, the accurate examination of which could hardly have failed to reveal to him the fundamental error underlying his investigation.

The necessity of a re-examination of these products is therefore evident, and at Dr. Roscoe's request I have carried out an investigation of the whole subject of the compounds formed by vanadium and sulphur, the results of which I have now the honour to lay before the Chemical Society.

# Method of Analysis.

Before proceeding to give the experimental details, it will be convenient to describe shortly the method devised for the analysis of these compounds of vanadium and sulphur, especially as the process is equally applicable to the analysis of other sulphides, which, when heated in a stream of air or oxygen, give off all their sulphur as sulphur dioxide, leaving a residue of metallic oxide.

The substance to be analysed is weighed out into a tared porcelain boat, and this is transferred to a hard glass tube contained in an ordinary combustion furnace. The end of the tube nearest which the boat is placed is connected with a gas apparatus supplying pure air or oxygen (preferably the latter), whilst the other end is drawn out and attached to two series of potash-bulbs, the first of which contains strong bromine-water, whilst the second is filled with distilled water.

A slow current of oxygen is allowed to pass through the apparatus, and the tube is heated, first at some little distance behind the boat, the heat being afterwards gradually extended to that part of the tube in which the substance is placed. Any free sulphur which volatilises may be burnt to dioxide by first heating the tube in front and then very gradually extending the heat backwards, when the sulphur is completely burnt in passing through the heated portion of the tube. The sulphur dioxide is swept forward into the bromine-bulbs and there completely oxidised, whilst a residue of pure vanadium pentoxide remains in the boat, and from its weight the amount of vanadium present is readily ascertained.

During the progress of the experiment bromine-vapours are carried forward by the stream of gas and absorbed by the water contained in the second set of bulbs. Not only is the greater part of the brominevapour thus kept from passing into the air, but the absorption of every trace of sulphur dioxide is secured by the gas passing through this second series of bromine-bulbs.

In the combustion of the sulphur a small quantity of sulphur trioxide is always formed, and this combined with a trace of water, which is invariably present, remains as sulphuric acid in the combustion-tube. At the conclusion of the experiment the boat containing the pentoxide is removed and weighed. The contents of the bulbs, together with the washings of the combustion-tube, are transferred to a flask and boiled until the excess of bromine is driven off, a small funnel being placed in the neck of the flask to prevent loss by spirting.

A solution is thus obtained containing all the sulphur as sulphuric acid, together with some hydrobromic acid formed during the oxida-

tion of the sulphur dioxide, and in this the sulphuric acid is determined by precipitation in the usual way.

The following numbers obtained in the combustion of pure sulphur show that the method is a reliable one :---

(a.)	) 0 <sup>.</sup> 2034 s	ubstance	gave 1.4820 B	aSO₄.
(b.)	0.1696	,,	1.2314	<b>27</b>
(c.)	0.1766	,,	1.2856	"
(a.)	( <i>b</i> .)	(c.)	Mean.	
100.18	99.82	100.06	100.02 per	cent. of S.

### EXPERIMENTS ON BERZELIUS'S COMPOUNDS.

As has been stated, Berzelius in his paper on the vanadium compounds describes two sulphides—the disulphide,  $VS_2$ , and the persulphide,  $VS_3$ ; and these corrected for his omission of oxygen and for the alteration in the atomic weight of vanadium would now be written  $(V_2O_2)S_2$  and  $(V_2O_2)S_3$ . As, however, these have generally been described as  $V_2S_4$  and  $V_2S_5$ , the question as to what is their true constitution has yet to be decided. Berzelius states that both these compounds may be obtained by precipitation in the wet way, and that one of them, the bisulphide, can also be prepared by a dry process. For a reason, which will be afterwards apparent, these two methods will be treated separately.

## (1.) Berzelius's Persulphide obtained by Precipitation.

In the preparation of this and the succeeding compound Berzelius's methods have been generally followed, special precautions against oxidation having in addition been adopted. The persulphide was prepared by saturating sodium vanadate with sulphuretted hydrogen and pouring the resulting liquid into an excess of dilute sulphuric or hydrochloric acid diluted with ten volumes of water. The precipitate formed, after washing in the cold with sulphuretted hydrogen water and drying in an atmosphere of carbon dioxide, was found to contain a large quantity of sulphur, a fact not mentioned by Berzelius. This was removed by washing with hot carbon disulphide, the operation being carried out in a funnel surrounded by a water-jacket kept at a temperature of 50° by a current of steam. The top of the funnel was closed by a glass plate, through a circular hole in the centre of which the delivery tube of a stoppered glass globe containing the carbon disulphide passed, and thus by regulating the flow of the liquid the hot disulphide percolated slowly through the substance under treat-The sulphide thus purified, after drying at 120° in an atmoment.

sphere of carbon dioxide until its weight was constant, was found still to retain water of hydration amounting to from 5 to 7 per cent.

For purposes of analysis the vanadium and sulphur were determined by the method already described. The water was estimated by combustion with lead oxide and the oxygen determined by difference.

Of the following preparations No. 1 was obtained by precipitation with sulphuric acid, and Nos. 2 and 3 by precipitation with hydrochloric acid :---

- No. 1. 0.2312 substance gave 0.1499  $V_2O_5$  and 0.7594 BaSO<sub>4</sub>; 0.4042 substance gave 0.0236  $H_2O$ .
- No. 2. 0.2428 substance gave  $0.1402 V_2O_5$  and  $0.8440 BaSO_4$ ; 0.3906 substance gave  $0.0264 H_2O$ .
- No. 3. 0.2464 substance gave 0.1602  $\rm K_2O_5$  and 0.7686 BaSO<sub>4</sub>; 0.4198 substance gave 0.0190 H<sub>2</sub>O.

From these numbers the composition of the anhydrous compounds is found to be as follows, the calculated composition of  $(V_2O_2)S_3$  and  $V_2S_5$  being appended for purposes of comparison:—

	No. 1.	No. 2.	No. 3.	Mean.	$(V_2O_2)S_3.$	$V_2S_5$ .
V	38.70	34.81	38.25	37.25	$44 \cdot 44$	39.04
S	47.95	51.28	44.91	48.05	41.67	60.96
0	13.35	13.91	16.84	14.70	13.89	

These numbers show that the product is an oxy-compound, but they do not warrant the assumption of the formula  $(V_2O_2)S_3$ . Indeed the variable composition of the precipitate precludes the assignment to it of any definite formula.

## (2.) Berzelius's Bisulphide obtained by Precipitation.

In the preparation of this compound the pentoxide was dissolved in hydrochloric acid, the excess of acid removed by evaporation, water added, the vanadium reduced by sulphuretted hydrogen, and the precipitated sulphur removed by filtration. Freshly prepared ammonium hydrosulphide was then added in excess and the resulting liquid poured into an excess of dilute sulphuric or hydrochloric acid. The precipitates thus obtained were purified and analysed as described under the foregoing compound.

Of the following preparations Nos. 1 and 2 wore prepared by precipitation with sulphuric acid, and Nos. 3 and 4 by precipitation with hydrochloric acid :—

- No. 1. 0.2116 substance gave 0.1168  $V_2O_5$  and 0.8668 BaSO<sub>4</sub>; 0.2846 substance gave 0.0114 H<sub>2</sub>O.
- No. 2. 0.2133 substance gave  $0.1353 V_2O_5$  and  $0.7210 BaSO_4$ ; 0.3352 substance gave  $0.0168 H_2O$ .

- No. 3. 0.2113 substance gave 0.1227  $\nabla_2O_5$  and 0.8254 BaSO<sub>4</sub>; 0.3235 substance gave 0.0138 H<sub>2</sub>O.
- No. 4. 0.2056 substance gave  $0.1322 V_2O_5$  and  $0.6578 BaSO_4$ ; 0.2960 substance gave  $0.0182 H_2O$ .

The following numbers give the composition of the anhydrous compounds, the percentage numbers for  $(V_2O_2)S_2$  and  $V_2S_4$  being added for comparison :---

	No. 1.	No. 2.	No. 3.	No. 4.	Mean.	$(V_2O_2)S_2.$	$V_2S_4$ .
v	32.31	37.53	34.08	38.49	35.60	51.61	44.46
s	58.66	48.93	56.10	46.86	52.64	32.26	55.54
0	9.03	13.54	9.82	14.65	11.76	16.13	

As in the case of the preceding compound, this product is clearly an oxysulphide which does not correspond to the formula generally assigned to it, nor indeed does its variable composition permit of its being represented by any formula whatever.

It may be remarked that in Berzelius's original paper there is no evidence that these products were submitted to analysis, the formulæ assigned to them by him being simply such as he believed them to possess considering the mode of their preparation.

I purpose subjecting these compounds obtained by precipitation to further examination with the object of determining if possible the conditions which govern the variations in the character of the precipitates, and of ascertaining whether they contain or can be converted into any oxysulphide having a simple and definite formula.

# (3.) Berzelius's Bisulphide obtained in the Dry Way.

With respect to this preparation Berzelius observes:—"When vanadium suboxide [the trioxide] is heated to full redness in sulphuretted hydrogen, it is decomposed by the gas, water and hydrogen are evolved, and the mass finally gains so much in weight as corresponds to 2 atoms of sulphur to 1 atom of metal" (*Pogg. Ann.*, **22**, 19). This reaction would be expressed by the following equations, in which  $(V_2O_2)$  is the equivalent of Berzelius's metal :—

(a.) 
$$(V_2O_2)O + H_2S = (V_2O_2)S + H_2O.$$
  
(b.)  $(V_2O_2)S + H_2S = (V_2O_2)S_2 + H_2.$ 

A careful re-examination of this reaction yielded results as unexpected as they are interesting. A weighed quantity of vanadium pentoxide was reduced at redness in a stream of pure hydrogen, until its weight was constant, and the loss corresponded to a reduction of  $V_2O_5$  to  $V_2O_3$ . This product was then heated in  $H_2S$  at redness, and the product from time to time weighed. It required five to six successive

heatings of three hours each before the weight became constant. The gain of weight then corresponded fairly to a conversion of  $V_2O_3$  into  $(V_2O_2)S_2$ . This calculated gain is 32 per cent.; the experimental numbers in three cases were, 34.9, 34.5, and 35.0. The product thus obtained was, however, on examination found to contain *no oxygen*, giving on analysis the following numbers, which show it to be vanadium trisulphide,  $V_2S_3 :=$ 

No. 1.	0.2408	substanc	e gave	0.2162	$V_2O_5$	and	0.8625	BaSO4
No. 2.	0.2456	,,	-	0.2202	,,	,	0.8776	,,
No. 3.	0.2404	,,		0.2164	,	,	0.8498	"
		No. 1.	No. 2.	No.	3.	Mea	n.	$V_2S_3$ .
<b>v</b>		50· <b>4</b> 7	50.37	50.5	59	50.4	48	51.62
<b>S</b>		49.26	49.12	48.0	61	48.9	99 4	<b>4</b> 8 <b>·3</b> 7

The formation of the sulphide is therefore the result of the following simple reaction :---

$$V_2O_3 + 3H_2S = V_2S_3 + 3H_2O_1$$

On comparing this equation with those already given as embodying Berzelius's explanation of the reaction which here takes place, it is apparent that the percentage gain of  $V_2O_3$  in passing into  $V_2S_3$  is identical with that which would ensue on its passage into  $(\nabla_2O_2)S_2$ , and, moreover, that the percentage amounts of vanadium in the products would be the same in both cases.

The difference between the two substances, however, at once becomes evident when the amount of sulphur present in them is determined, and had Berzelius made a complete analysis of the product, he would have obtained percentage numbers adding up to 116, due to his calculating from the weight of  $V_2O_5$  the weight of his supposed metal (in fact,  $V_2O_2$ ) present. He would thus have been led into an inquiry which would in all probability have resulted in his ascertaining the true nature of metallic vanadium and of the vanadium compounds.

I shall now proceed to a systematic description of the results I have obtained as to the methods of preparation and properties of the compounds of

## VANADIUM AND SULPHUR.

Vanadium forms three sulphides, corresponding with three of the four distinctly characterised oxides of vanadium :----

Sulphides.		Oxides.	
Vanadium disulphide	$V_2S_2$	Vanadium dioxide	$V_2O_2$
Vanadium trisulphide	$V_2S_3$	Vanadium trioxide	$V_2O_3$
_		Vanadium tetroxide	$V_2O_4$
Vanadium pentasulphide.	$V_2S_5$	Vanadium pentoxide	$V_2O_5$

# (1.) Vanadium Disulphide, $V_2S_2$ .

The lowest oxide of vanadium which can be obtained by reduction in hydrogen at redness is the trioxide,  $V_2O_3$ . In the sulphur series, however, the reducing action of hydrogen proceeds further, notwithstanding the fact that sulphuretted hydrogen is a much less stable compound at a red heat than is the vapour of water.

When the trisulphide of vanadium, which will be next described, is heated to intense redness in hydrogen, sulphuretted hydrogen is slowly evolved, and a reduction to disulphide gradually takes place. In carrying out this experiment, which lasts from four to eight days, according to the quantity experimented on, the greatest care has to be taken that the hydrogen is perfectly dry, and is absolutely free from occluded oxygen, as the sulphide is oxidised with the greatest readiness and the results are thus vitiated. In the preparation of this sulphide, all the precautions have to be adopted that were described by Roscoe for the preparation of metallic vanadium. The hydrogen generator is a continuous one, in which, by a supply of dilute sulphuric acid at the top, and a withdrawal of zinc sulphate solution at the bottom of the generator, an uninterrupted stream of hydrogen may be obtained for many days in succession. The gas is purified by passing through wash-bottles, the first containing alkaline lead acetate solution, the second silver nitrate solution, and the three following ones boiled sulphuric acid; the hydrogen then passes through a long horizontal tube containing pumice-stone moistened with boiled sulphuric acid; it is next passed over a column of heated spongy platinum, where any trace of occluded oxygen is converted into water, and this is again absorbed by a second pumice and sulphuric acid tube. All the india-rubber joints are soaked in melted paraffin, and put on hot, then wrapped with copper wire, and finally covered with melted paraffin. At the point where the hydrogen delivery tube is connected with the porcelain tube containing the substance, the junction is surrounded by a jacket filled with melted paraffin. The material is contained in a porcelain or platinum boat, and the porcelain tube carrying this is heated to very intense redness at the full heat of a Hofmann's gas furnace. When the apparatus has to be left over night, a slow stream of hydrogen is allowed to pass continuously through the apparatus, and on re-commencing the experiment, the spongy platinum is heated for some time before the furnace is lighted.

The sulphuretted hydrogen, which is at first evolved with fair rapidity, gradually diminishes in quantity, and at last the amount becomes very small indeed; but in no case have I succeeded in getting rid of the last traces of sulphur, even after 72 hours' heating at the highest temperature of the Hofmann furnace.

The percentage loss, as well as the analytical numbers, whilst agreeing fairly well with the calculated amounts, still show that a small portion of the trisulphide is not completely reduced to disulphide. The calculated percentage loss of sulphur is 16.5; the actual loss of 0.86 gram, after heating for 25 hours, was 15.5 per cent. In the following cases the composition of several preparations of disulphide are given. No. 1 was heated 25 hours; No. 2, 22 hours; No. 3, 40 hours; and No. 4, 72 hours:—

	No. 1.	0.2042	substance	gave 0.2116	$\rm V_2O_5$ and	0.5976	$BaSO_4$
	No. 2.	0.2446	,,	0.2540	,,	0.7244	,,
	No. 3.	0.2554	,,	0.2662	"	0.7416	,,
	No. 4.	0.2198	,,	0.2308	,,	0.6437	,,
		No. 1.	No. 2.	No. 3.	No. 4.	Mean.	$V_2S_2$ .
V		58.24	58.34	58.57	59.00	58.54	61.23
s.		40.24	40.70	39.93	40.27	40.28	38.46

The disulphide forms glistening black scales, having a slight bronze lustre, or a brownish-black powder, according as it is prepared from the scaly or powdery trisulphide. The specific gravity of the scaly form is 4.2, and that of the powder, 4.4. When heated it unites with oxygen with the greatest avidity. A specimen of the disulphide, which after moistening with water, had been dried at about  $130^{\circ}$  in carbon dioxide, was taken out into the air whilst hot, and then absorbed oxygen so rapidly, that it became incandescent, and sulphur dioxide was evolved. When heated in the air, sulphur dioxide is given off, whilst the substance passes through the stages of blue and black oxide into the fused crystalline pentoxide. If it be heated in a limited supply of air, free sulphur is also given off, the oxygen being retained by the vanadium.

Boiling hydrochloric acid, both strong and dilute, and boiling dilute sulphuric acid attack the disulphide but very slightly; cold strong sulphuric acid does not act upon it, but it is dissolved by the hot acid to a greenish-yellow solution. Dilute nitric acid attacks the sulphide slowly, the solution being coloured blue; with the hot dilute acid the action is more rapid, whilst by the strong hot acid the substance is violently oxidised, and the solution contains vanadic sulphate.

Caustic soda and ammonia attack the vanadium sulphide but slightly, either in the cold or on heating; yellow ammonium sulphide slowly dissolves the disulphide forming a wine-red solution, whilst in the case of the freshly prepared colourless ammonium hydrosulphide the liquid acquires a splendid purple tint. Potassium hydrosulphide acts slowly on the disulphide, yielding a violet-red solution.

## (2.) Vanadium Trisulphide, V<sub>2</sub>S<sub>3</sub>.

This is the most important sulphide of vanadium, as it forms the

starting point for the preparation of the other sulphides. It also possesses a special interest as being the only pure non-oxygenated vanadium compound obtained by Berzelius, in his investigation of this metal and its compound.

Vanadium trisulphide is produced in the following methods :----

(1.) By the action of sulphuretted hydrogen on the trioxide at redness. This reaction was described by Berzelius, and has already been fully considered (see p. 732).

It is, however, not necessary to prepare the trioxide for this purpose, as sulphuretted hydrogen acts similarly on the pentoxide. The first action is a reduction of the pentoxide to trioxide, this being evident from the fact that the pentoxide first loses, and afterwards gains in weight.

That the product is the trisulphide will be seen from the following analysis of a preparation obtained by heating the pentoxide to full redness in sulphuretted hydrogen for 13 hours.

0.2265 gram gave 0.2073 V2O5, and 0.7870 BaSO4.

		$\nabla_2 S_3$ .
V	51.42	51.62
S	47.77	48.37

(2.) Vanadium trisulphide is also formed by the action of sulphuretted hydrogen at redness on any chloride of vanadium, or on vanadyl trichloride,  $VOCl_3$ . It was by this reaction that I first obtained a true sulphide of vanadium, for after convincing myself that Berzelius's precipitation products were oxy-compounds, I sought for a new method of preparing the sulphides. This mode of production by means of the chlorides is not, however, suitable for the preparation of the sulphide in quantity, as the chlorides of vanadium are prepared only with considerable difficulty. Sulphuretted hydrogen attacks the liquid tetrachloride in the cold; the substance becomes very hot, and the trichloride is formed with separation of sulphur and evolution of hydrochloric acid:—

 $2\mathrm{VCl}_4 + \mathrm{H}_2\mathrm{S} = 2\mathrm{VCl}_3 + 2\mathrm{HCl} + \mathrm{S}.$ 

The dichloride and trichloride of vanadium are not attacked until a temperature approaching redness is attained. At full redness the action proceeds rapidly, hydrochloric acid is evolved, and the trisulphide is formed, irrespective of the special chloride which is subjected to the reaction.

This is seen from the following analytical data :---

No. 1. 0 <sup>.</sup> 2	2048 gram	gave	0.1794	$V_2O_5$	and 0.7235	$BaSO_4$
No. 2. 0 <sup>.</sup> 1	1980 ັ	"	0.1706	,,	0.6992	,,
No. 3. 0.2	2041	,,	0.1815	,,	0.7275	•,
No. 4. 0.2	2060	,,	0.1832	,,	0.7340	,,
No. 5. 0.2	2101	,,	0.1868	,,	0.7560	,,

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	
	From VCl <sub>2</sub> .	From amor- phous VCl <sub>3</sub> .	From scaly VCl <sub>3</sub> .	From VCl <sub>4</sub> .	From VOCl <sub>3</sub>	$V_{2}S_{3}$ .
v	49.23	48.41	49.90	49.98	49.97	51.62
S	48.57	48.59	49.02	48.99	49.48	48.37

(3.) Vanadium trisulphide is directly produced from the pentoxide by the action of carbon disulphide vapour at redness. This method 1 have found to be the most convenient for the preparation of the trisulphide in quantity. The operation is conducted as follows. A slow current of pure dry carbon dioxide is passed through carbon disulphide contained in a flask heated in a water-bath, the temperature of which is maintained by a jet of steam. The carbon dioxide charged with the disulphide vapour then passes over the pentoxide, contained in a hard glass tube, placed in a combustion furnace. The posterior end of the combustion-tube is drawn out and connected with a condenser for the recovery of the excess of carbon disulphide. The air in the apparatus is first displaced by carbon dioxide, and the pentoxide in the furnace is then heated to redness, whilst the temperature of the water-bath is raised to 50° and maintained at this temperature, the current of carbon dioxide being allowed to pass but slowly. In this way a slow passage of carbon disulphide vapour is obtained through the apparatus, and a steady condensation of carbon disulphide takes The reaction commences readily, and place at the posterior end. large quantities of sulphur are deposited and sulphur dioxide evolved. Carbon dioxide is no doubt also formed in the reaction, but the conditions of the experiment do not permit of the direct observation of this fact. By this method 20 grams of pentoxide may be converted into sulphide in from six to ten hours. The condensed carbon disulphide after rectification over lime may be again used for the preparation of the trisulphide.

The following numbers were obtained in analyses of four preparations thus obtained :---

- No. 1. (a.) 0.1999 substance gave 0.1816 V<sub>2</sub>O<sub>5</sub> and 0.6977 BaSO<sub>4</sub>. (b.) 0.1999 , 0.1810 , ; 0.2024 substance
  - gave 0.7062 BaSO<sub>4</sub>.

No. 1.

- No. 2. 0.2731 substance gave 0.2472  $V_2O_5$ ; 0.2001 substance gave 0.6934 BaSO<sub>4</sub>.
- No. 3. 0.1678 substance gave  $0.1518 V_2O_5$ , and  $0.5828 BaSO_4$ .

No. 4. 0.2173 ,, 0.1977 ,, 0.7569 ,,

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	(a.)	(b.)	No. 2.	No. 3.	No. 4.	Mean.	$V_2S_3$ .
<b>V</b>	51.04	50.88	50.87	50.83	51.13	50.95	51.62
$\mathbf{s}\ldots$	47.97	47.97	47.64	47.75	47.88	47.84	<b>4</b> 8·37

Vanadium trisulphide forms either glistening black scales with graphitic lustre, or a grey-black amorphous powder, according as it is prepared from the scaly chlorides on the one hand or from the oxide on the other. The specific gravity of the scaly product is 3.7, and that of the amorphous powder 4.0. Heated in air or oxygen the trisulphide is oxidised similarly to the disulphide, but much less readily. Sulphur dioxide is evolved, and the blue and black oxides formed, these gradually passing into the pentoxide.

The trisulphide is but slightly attacked by dilute or strong hydrochloric acid, either in the cold or on heating. Hot dilute sulphuric acid also acts upon it but slowly, but by the strong and hot acid it is more rapidly dissolved. Dilute nitric acid acts upon the trisulphide slowly in the cold, and more rapidly on heating, forming a blue solution, as in the case of the disulphide; by the strong acid it is readily oxidised in the cold, whilst in the case of the hot acid the oxidation proceeds with violence.

Caustic soda and ammonia have a slight solvent action on the trisulphide. Yellow ammonium sulphide acts upon the substance slowly, forming a wine-red liquid; whilst with the colourless ammonium hydrosulphide a splendid purple-coloured solution is obtained, identical in appearance with that formed in the case of the disulphide. The colour of the liquid produced on solution in potassium hydrosulphide is violet-red.

## Vanadium Pentasulphide, $V_2S_5$ .

At a temperature of about 400°, vanadium trisulphide takes up two additional atoms of sulphur, forming the pentasulphide,  $\nabla_2 S_5$ . For the preparation of this compound the trisulphide is mixed with onethird its weight of sulphur (purified by carbon disulphide), the mixture very finely powdered and placed in a strong narrow tube. The tube, after filling with dry carbon dioxide, is temporarily closed by a cork provided with a narrow capillary tube (to prevent access of oxygen), and the tube is then sealed off as near as possible to the surface of the mixture. The sealed tube is next heated in a hot-air oven for three hours, to a temperature of about 400° (cadmium iodide melting at 404° being used as an indicator). The product, after washing with hot carbon disulphide to remove any free sulphur present, leaves a residue of the pure pentasulphide.

It is inadvisable to use a large excess of sulphur in the preparation of this sulphide, for although the pentasulphide is produced, it retains from 1 to 2 per cent. of sulphur very tenaciously, and the removal of this is a matter of considerable difficulty.

The following table gives the composition of specimens of pentasulphide prepared as before described :---

No. 1. 0.1709 substance gave  $0.1139 V_2O_5$  and  $0.7526 BaSO_4$ . No. 2. 0.1770 ,, 0.1180 ,, 0.7908 ,, No. 3. 0.1755 ,, 0.1220  $V_2O_5$ ; and 0.1740 substance gave 0.7507 BaSO<sub>4</sub>.

	No. 1.	No. 2.	No. 3.	Mean.	$V_2S_5$ .
v	37.46	37.46	39.07	38.00	39.04
s	60.56	61.42	59.33	60.44	60.96

Vanadium pentasulphide forms a black powder, having a specific gravity of 3.0. Heated in the air it gives off sulphur dioxide, and is converted into the black oxide, which on further heating passes into the fused pentoxide. If, however, the heat be very carefully applied, some free sulphur is first given off without this taking fire. Heated in a neutral atmosphere, the pentasulphide loses two atoms of sulphur, being converted into trisulphide.

The pentasulphide is but slightly attacked by hot strong hydrochloric acid, and by hot dilute sulphuric acid, whilst by strong sulphuric acid it is slowly dissolved, forming a yellow solution. Hot dilute nitric acid dissolves the pentasulphide slowly, but completely; whilst by the strong acid it is more energetically oxidised.

Ammonia does not easily attack the pentasulphide, but it is readily dissolved by caustic soda, especially on heating, forming a yellow solution. In this respect it differs markedly from the other vanadium sulphides which dissolve but slightly in caustic soda. The pentasulphide is slowly acted upon by the alkaline sulphides. With colourless ammonium hydrosulphide the solution has the splendid purple colour also vielded by the other vanadium sulphides. To obtain this colour in perfection, it is necessary that the hydrosulphide solution shall be completely saturated with sulphuretted hydrogen, and the colour is best obtained by passing sulphuretted hydrogen to excess through ammonia solution containing the pentasulphide in suspension. If the sulphuretted hydrogen be not present in excess, the liquid has a rich The solution of pentasulphide in yellow ammocarmine-red colour. nium sulphide is a brownish-red, whilst that in potassium hydrosulphide is wine-red.

#### Summary.

The foregoing experiments show :---

(1.) That the precipitation products obtained by Berzelius are oxycompounds, not corresponding either with the formulæ  $V_2S_4$  and  $V_2S_5$ , or with those  $V_2O_2S_2$  and  $V_2O_2S_3$ .

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(2.) That the substance obtained by him in the dry way is a true sulphide of vanadium, being the trisulphide,  $V_2S_3$ .

(3.) That, in addition to the trisulphide, two other vanadium sulphides exist, namely, the disulphide,  $V_2S_2$ , and the pentasulphide,  $V_2S_5$ .

(4.) That compared with the oxides, the sulphides of vanadium are compounds of inferior stability; for whilst in the oxygen series the penta-compound is stable at redness in a neutral atmosphere, in the sulphur series the penta- is converted into the tri-sulphide. Again, in hydrogen at intense redness, the trioxide is permanent; whilst the trisulphide is under similar conditions reduced to disulphide.